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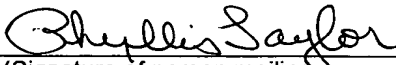
APPLICATION FOR UNITED STATES PATENT

**HYDROCARBON SYNTHESIS PROCESS USING PRESSURE SWING
REFORMING**

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CROSS REFERENCE TO RELATED APPLICATION:

This application is a Continuation-in-Part of Non-Provisional Application No. 10/756,651 filed January 13, 2004 which is based on Provisional Application No. 60/450,902 filed February 28, 2003.

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CASE NO. JJD-0404



27810

PATENT TRADEMARK OFFICE

**HYDROCARBON SYNTHESIS PROCESS USING PRESSURE SWING
REFORMING**

5 **[0001]** This application claims the benefit of U.S. Provisional Application
No. 60/450,902 filed February 28, 2003.

Field of the Invention

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[0002] The present invention relates to process improvements in synthesizing hydrocarbon compounds from synthesis gas. More particularly, the invention relates to a process scheme wherein synthesis gas is produced in a cyclic packed-bed operation in which the reforming cycle of the synthesis gas production is performed at a higher pressure than the regeneration cycle and in which light gas and steam from the hydrocarbon synthesis process is used in the reforming cycle.

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Background of the Invention

[0003] Conventional synthesis gas generating processes include steam reforming, gas phase partial oxidation and autothermal reforming. Each of these processes has advantages and disadvantages when compared to each other.

25 **[0004]** In a steam reforming process, steam is reacted with a hydrocarbon containing feed to produce a hydrogen-rich synthesis gas. The general stoichiometry, as illustrated for methane, is:



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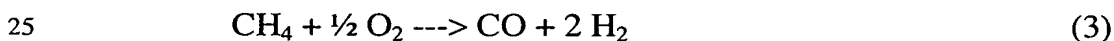
Typically, an excess of steam is used to drive the equilibrium to the right. As applied to hydrogen manufacture, excess steam also serves to increase water gas shift:



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[0005] Because of the high endothermicity of the reaction, steam reforming is typically carried out in large furnaces, in which the catalyst is packed into tubes. The tubes must withstand the high pressure of the produced synthesis gas, while transmitting heat at temperatures approaching 1000°C. As described in Stanford
10 Research Institute International Report No. 148A (1995), steam reforming process efficiency, defined as the heat of combustion of product synthesis gas divided by the heat of combustion of reforming feed and furnace fuel, is approximately 79%, while the space velocity, defined as Standard Cubic Feet per Hour of C₁-equivalent feed / ft³ of catalyst bed is 690 hr⁻¹. Unfortunately,
15 steam reforming furnaces occupy a very large volume of space, orders of magnitude greater than the tube volume, such that low productivity limits the economic attractiveness of the process.

[0006] The gas phase partial oxidation process involves the partial oxidation
20 of the hydrocarbon containing feed in the gas phase. The feed components are introduced at a burner where they combust with sub-stoichiometric oxygen to produce a synthesis gas mixture. The ideal gas phase partial oxidation reaction, as illustrated for methane, is:



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However, gas-phase reaction kinetics tend to over-oxidize some of the feed, resulting in excessive heat generation and substantial yield of H₂O, CO₂, and unreacted hydrocarbons that may leave the reactor as soot.

[0007] For these reasons, when gas phase partial oxidation chemistry is applied to clean feeds, it is preferred to add steam to the feed and add a bed of steam reforming catalyst to the bottom of the gas phase partial oxidation reactor vessel. This combination of gas phase partial oxidation and steam reforming is called autothermal reforming. The heat needed for steam reforming is provided in-situ from the excess heat generated by the gas phase partial oxidation reactions.

[0008] Autothermal reforming can be substantially more compact than steam reforming because furnaces are not used to provide heat of reaction. Embodiments of autothermal reforming presently under development for gasoline-powered fuel cell vehicles make use of a catalytic partial oxidation step, which can impart even greater compactness to the autothermal reforming process. The thermal efficiency of autothermal reforming reactors are generally in the range of 90%. While autothermal reforming based on catalytic partial oxidation may have high productivity (gas hourly space velocity on order of 10^4 as C_1 -equiv.), conventional partial oxidation-based autothermal reforming has a space velocity very similar to that of steam reforming (about 10^3 hr^{-1}). However, autothermal reforming requires a source of oxygen. In the fuel cell vehicle case, this oxygen is typically provided as low-pressure air, which results in a nitrogen-diluted, low-pressure synthesis gas, while in refinery or chemicals embodiments, this oxygen is typically provided as purified O_2 , and the cost of air separation can be greater than the cost of the autothermal reforming process.

[0009] Sederquist (U.S. Pat. Nos. 4,200,682, 4,240,805, 4,293,315, 4,642,272 and 4,816,353) teaches a steam reforming process in which the heat of reforming is provided within the bed by cycling between combustion and reforming stages of a cycle. As described by Sederquist, the high quality of heat recovery within

the reforming bed results in a theoretical efficiency of about 97%. However, the examples and commercial projections within these patents describe a process that operates at very low productivity, with space velocities of around 95 hr^{-1} (as C_1 -equiv). Moreover, this process requires a compressor to compress the product synthesis gas to useful pressures for hydrocarbon synthesis.

[0010] Recently a highly efficient and highly productive process for producing synthesis gas in a cyclic, packed-bed operation has been discovered. In this process, the reforming step involves preheating a first zone to a temperature in the range of about 700°C to 2000°C and then introducing a 20°C to 600°C hydrocarbon-containing feed, along with steam and optionally CO_2 to the inlet of the first zone. Upon introduction of the reactants, the hydrocarbon is reformed into synthesis gas over a catalyst in this first zone. The synthesis gas is then passed from the first zone to a second zone, where the gas is cooled to a temperature close to the inlet temperature of the hydrocarbon feed. The synthesis gas is recovered as it exits the inlet of the second zone.

[0011] The regeneration step begins when a gas is introduced to the inlet of the second zone. This gas is heated by the stored heat of the second zone to the high temperature of the zone and carries the heat back into the first zone. Finally, an oxygen-containing gas and fuel are combusted near the interface of the two zones, producing a hot flue gas that travels across the first zone, thus reheating that zone to a temperature high enough to reform the feed. Once heat regeneration is completed, the cycle is completed and reforming begins again.

[0012] An advantage of this process is the ability to operate the reforming step at a higher pressure than the regeneration step, thus creating a pressure swing, and producing high pressure synthesis gas.

[0013] Processes for producing liquid and gaseous hydrocarbon products from synthesis gas are known. These include Fischer-Tropsch synthesis, methanol synthesis and hydroformylation. Each of these are exothermic processes that operate best at a $H_2:CO$ molar ratio of about 2.

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[0014] Fischer-Tropsch synthesis typically is carried out using a cobalt or iron catalyst at temperatures of between $200^{\circ}C$ to $450^{\circ}C$ and pressures of between 10 and 300 atmospheres. The hydrocarbon product is roughly equivalent to a very paraffinic, natural petroleum oil that contains predominantly
10 straight chain, saturated paraffins, some olefins and less than about 1% alcohols, fatty acids and other oxygenates.

[0015] Methanol synthesis typically is carried out using copper-zinc oxide-alumina catalysts at pressures of about 50 - 100 atm. and temperatures of about
15 $200^{\circ}C$ - $300^{\circ}C$. The by-products of methanol synthesis includes ethers, formates, ketones, hydrocarbons, and higher alcohols.

[0016] Hydroformylation involves the reaction of olefins with CO and H_2 and typically is carried out in the liquid phase in the presence of a metal carbonyl
20 catalyst at temperatures in the range of $50^{\circ}C$ to $200^{\circ}C$ at pressures of 10 to 200 atm.

[0017] The practical application of any synthesis gas production technique or hydrocarbon conversion process will depend upon how well the upstream and
25 downstream processing systems can be integrated into an overall process design. The invention described below and defined in the claims addresses practical process design and operating requirements that achieve effective integration of pressure swing reforming with downstream hydrocarbon conversion and that provides unanticipated advantages.

Summary of Invention

[0018] The present invention, in one aspect, provides an improvement in exothermic hydrocarbon synthesis processes that use synthesis gas, in which the
5 improvement comprises integrating pressure swing reforming with such a synthesis process whereby thermal and material efficiencies over conventional reforming are achieved. Thus in one embodiment at least some hydrogen which is produced in the pressure swing reforming process is removed from the synthesis gas and is combusted with air to provide the heat for the regeneration
10 step of the pressure swing reforming process. In another embodiment the exothermic synthesis process is cooled with water to produce steam which is used in the pressure swing reforming.

[0019] A preferred embodiment of the invention comprises:
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(a) introducing a feed stream comprising a hydrocarbon and steam through a first end of a first zone containing bed packing materials and a steam reforming catalyst to produce at a first pressure a product synthesis gas stream containing a ratio of $H_2:CO$ greater than 2:1,
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(b) passing at least a portion of the product to step (a) to a second zone containing bed packing materials, and transferring the sensible heat from the product to the packing materials;

25 (c) removing substantially all of the product from said second zone;

(d) introducing an oxygen-containing gas into a second end of said second zone;

(e) contacting said oxygen-containing gas with a fuel and combusting said gas and fuel within said zones at a second pressure lower than the first pressure, thereby re-heating said first zone to reforming temperatures and creating a fluegas which exits through the first end of said first zone;

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(f) separating sufficient hydrogen from the product recovered in step (c) to produce a synthesis gas stream having a $H_2:CO$ ratio of about 2:1;

(g) using separated hydrogen of step (b) as fuel in step (e); and

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(h) introducing the synthesis gas of step (f) into a hydrocarbon synthesis reactor for conversion therein to liquid products.

The embodiments of the invention are set forth in the detailed description hereinafter.

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Brief Description of Drawings

[0020] Figures 1a and 1b are schematic illustrations showing the basic reforming and regeneration steps of pressure swing reforming.

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[0021] Figure 2 is a schematic illustration of a basic two cycle pressure swing reforming process employing heat exchange.

[0022] Figures 3 to 5 are schematic illustrations of a process designs employing pressure swing reforming and hydrocarbon synthesis.

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Detailed Description

[0023] The basic two-step cycle of pressure swing reforming is depicted in Figure 1. Referring now to Figures 1a and 1b, a first zone, or reforming zone (1),

called a swing bed reformer, and a second zone, or recuperating zone, called a synthesis gas heat recuperator (7). The beds of both zones will include packing material, while the reforming bed (1) will include catalyst for steam reforming. Though illustrated as separate reforming and recuperating zones, it is to be
5 recognized that the pressure swing reforming apparatus may comprise a single reactor.

[0024] As shown in Figure 1a, at the beginning of the first step of the cycle, also called the reforming step, the reforming zone (1) is at an elevated
10 temperature and the recuperating zone (7) is at a lower temperature than the reforming zone (1). A hydrocarbon-containing feed is introduced via a conduit (15), into a first end (3) of the reforming zone (1) along with steam. The hydrocarbon may be any material that undergoes the endothermic steam reforming reaction including methane, petroleum gases, petroleum distillates,
15 kerosene, jet fuel, fuel oil, heating oil, diesel fuel and gas oil and gasoline. Preferably the hydrocarbon will be a gaseous material comprising methane and other normally-vapor phase hydrocarbons. Preferably, the steam will be present in proportion to the hydrocarbon in an amount that results in a steam to carbon ratio between about 1 and about 3 (considering only carbon in the hydrocarbon,
20 not carbon in CO or CO₂ species that may be present).

[0025] This feed stream picks up heat from the bed and is converted over the catalyst and heat to synthesis gas. As this step proceeds, a temperature profile (23) is created based on the heat transfer properties of the system. When the bed
25 is designed with adequate heat transfer capability, as described herein, this profile has a relatively sharp temperature gradient, which gradient will move across the reforming zone (1) as the step proceeds.

[0026] Synthesis gas exits the reforming bed (1) through a second end (5) at an elevated temperature and passes through the recuperating zone (7), entering through a first end (11) and exiting at a second end (9). The recuperating zone (7) is initially at a lower temperature than the reforming zone (1). As the
5 synthesis gas passes through the recuperating zone (7), the synthesis gas is cooled to a temperature approaching the temperature of the zone substantially at the second end (9), which is approximately the same temperature as the regeneration feed introduced during the second step of the cycle via conduit (19) (e.g. from about 20°C to about 600°C). As the synthesis gas is cooled in the
10 recuperating zone (7), a temperature gradient (24) is created and moves across the recuperating zone (7) during this step.

[0027] At the point between steps, the temperature gradients have moved substantially across the reforming zone (1) and the recuperating zone (7). The
15 zones are sized so that the gradients move across both in comparable time during the above reforming step. The recuperating zone (7) is now at the high temperature and the reforming zone (1) is at low temperature, except for the temperature gradient that exists near the exits of the respective zones. The temperature of the reforming zone (1) near the inlet end (3) has now been cooled
20 to a temperature that approaches the temperature of the hydrocarbon feed that has been entering via conduit (15) (e.g. from about 20°C to about 600°C).

[0028] In the practice of pressure swing reforming, there are alternative means for determining the end of the reforming step. Toward the end of the
25 reforming step, the temperature at end (5) of the reforming zone is reduced and consequently the reforming performance deteriorates below acceptable conversion efficiencies. Reforming performance, as used herein, refers to the conversion of feed hydrocarbons into synthesis gas components of H₂, CO and CO₂. The term percent conversion, as used herein, is calculated as the percent

conversion of the carbon in feed hydrocarbonaceous species into synthesis gas species of CO and CO₂. The term unconverted product hydrocarbons, as used herein, refers to product hydrocarbonaceous species that are not synthesis gas components of H₂, CO and CO₂. These typically include product methane, as well as feed hydrocarbons and the cracking products of feed hydrocarbons. The reforming step ends when the reforming performance deteriorates to a level that is below acceptable limits. In practice, optimization of the overall reforming and synthesis gas utilization process will dictate a desired, time-averaged level of reforming conversion. That time-averaged level of reforming conversion is typically greater than 80%, preferably greater than 90%, and most preferably greater than 95%.

[0029] The point in time at which the reforming step is ended, and thus the duration of the reforming step, may be chosen (a) as a response to the time-varying performance of the reformer during each reforming step; or (b) based on overall (time-averaged) performance or the system; or (c) fixed as a constant reforming step duration. In embodiment (a), at least one feature of the operation is monitored that is correlated to the reforming performance. This feature may be a composition such as CH₄, H₂, or CO, or alternatively a temperature, such as the temperature at the end (5) of the reforming bed. In one embodiment of the present invention, the reforming step is ended when the temperature at the end (5) of the reforming has decreased to a pre-selected temperature between about 700°C and about 1200°C. In embodiment (b), the reforming step duration is adjusted based on a measured feature that reflects the overall (time-averaged) performance or the system. This may be an average product composition such as CH₄, H₂, or CO. In one embodiment the present invention, the reforming step duration is adjusted based on the time-averaged concentration of CH₄ in the product, using control strategies known in the art to shorten or lengthen the duration to achieve a predetermined target CH₄ amount. In a preferred

embodiment, the target CH_4 amount is set at an amount that represents between about 1% and about 15% of the hydrocarbonaceous feed carbon. In case (c), the reforming step duration is of fixed length, at a value that is predetermined to be acceptable for the space velocity of the operation. In one embodiment the present invention, the reforming step duration is fixed at a duration between about 0.1 sec and less than about 60 seconds and preferably between about 1.0 and 30 seconds.

[0030] After the synthesis gas is collected via an exit conduit (17) at the second end (9) of the recuperating zone (7), the second step of the cycle, also called the regeneration step begins. The regeneration step, illustrated in Figure 1b, basically involves transferring the heat from the recuperator bed (7) to the reformer bed (1). In so doing, the temperature gradients 25 and 26 move across the beds similar to but in opposite directions to gradients 23 and 24 during reforming. In a preferred embodiment, an oxygen-containing gas and fuel are introduced via a conduit (19) into the second end (9) of the recuperating zone (7). This mixture flows across the recuperating zone (7) and combusts substantially at the interface (13) of the two zones (1) and (7). In the present invention, the combustion occurs at a region proximate to the interface (13) of the recuperation zone (7) and the reforming zone (1). The term, "region proximate", in the present invention, means the region of the PSR beds in which regeneration step combustion will achieve the following two objectives: (a) the heating of the reforming zone such that end (5) of the reforming zone is at a temperature of at least 800°C , and preferably at least 1000°C at the end of the regeneration step; and (b) the cooling of the recuperation zone to a sufficient degree that it can perform its function of accepting synthesis gas sensible heat in the subsequent reforming step. Depending on specific regeneration embodiments described herein, the region proximate to the interface can include from 0% to about 50% of the volume of the recuperation zone (7), and can

include from 0% to about 50% of the volume of the reforming zone (1). In a preferred embodiment of the present invention, greater than 90% of the regeneration step combustion occurs in a region proximate to the interface, the volume of which region includes less than about 20% the volume of the recuperating zone (7) and less than about 20% the volume of reforming zone (1).

[0031] The location of combustion may be fixed by introduction of one of the combustion components, e.g., the fuel, at or substantially at, the interface of the two zones (13), while the other component, e.g., the oxygen-containing gas may be introduced at the first end (9) of the recuperating zone (7). Alternatively, the fuel and oxygen-containing gas (19) streams may be mixed at the open-end (9) of the recuperating zone (7) and travel through the zone and combust at the interface of the zones (13). In this embodiment, the location of combustion is controlled by a combination of temperature, time, fluid dynamics and catalysis. Fuel and oxygen conventionally require a temperature-dependent autoignition time to combust. In one embodiment, the flow of a non-combusting mixture in a first substep of regeneration will set the temperature profile in the recuperating zone (7) such that the zone is not hot enough to ignite until the mixture reaches the interface of the zones.

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[0032] The presence of catalyst in the reforming zone can also be used to initiate combustion at that location, and a space between the reforming and recuperating zones can be added and designed to further stabilize the combustion process and confine the combustion to the area proximate to the above described interface. In yet another embodiment, the location of combustion is fixed by mechanical design of the recuperating zone. In this design, the fuel and oxygen-containing gas are travelling in separate channels (not shown), which prevent combustion until the feeds combine at the interface of the zones (13). At that

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location, flame holders (not shown) or a catalyst in the reforming zone will ensure that the combustion occurs.

[0033] The combustion of the fuel and oxygen-containing gas creates a hot
5 fluegas that heats the reforming zone (1) as the flue gas travels across that zone. The fluegas then exits through the first end of the reforming zone (3) via a conduit (27). The composition of the oxygen-containing gas/fuel mixture is adjusted to provide the desired temperature of the reforming zone. The composition and hence temperature is adjusted by means of the proportion of
10 combustible to non-combustible portions of the mixture. For example, non-combustible gases such as H_2O , CO_2 , and N_2 can be added to the mixture to reduce combustion temperature. In a preferred embodiment, non-combustible gases are obtained by use of steam, flue gas, or oxygen-depleted air as one component of the mixture. When the hot fluegas reaches the temperature
15 gradient within the reformer, the gradient moves further across the bed. The outlet temperature of the fluegas will be substantially equal to the temperature of the reforming zone (1) near the inlet end (3). At the beginning of the regeneration step, this outlet temperature will be substantially equal to the inlet temperature of the reforming feed of the preceding, reforming, step. As the
20 regeneration step proceeds, this outlet temperature will increase slowly and then rapidly as the temperature gradient reaches end (3), and can be 50-500°C above the temperature of the reforming feed by the end of the step.

[0034] In the practice of pressure swing reforming, there are alternative
25 means for determining the end of the regeneration step. The regeneration step ends when sufficient heat has been supplied or conveyed to the reforming bed to enable the carrying out of the reforming step. The point in time at which the regeneration step is ended, and thus the duration of the regeneration step, may be chosen (a) as a response to the time-varying performance of the PSR during each

regeneration step; or (b) based on overall (time-averaged) performance or the system; or (c) fixed as a constant regeneration step duration. In embodiment (a), some feature of the operation is monitored that is related to the regeneration performance. This feature could be a composition such as O_2 , CH_4 , H_2 , or CO ,
5 or could be a temperature such as the temperature at the end (3) of the reforming bed. In one embodiment of the present invention, the regeneration step is ended when the temperature at the end (3) of the reforming bed has increased to a pre-selected temperature between about $200^{\circ}C$ and about $800^{\circ}C$. In embodiment (b), the regeneration step duration is adjusted based on a measured feature that
10 reflects the overall (time-averaged) performance of the system. This feature may be an average product composition such as CH_4 , H_2 , or CO , or some other system measurement. In one embodiment of the present invention, the regeneration step duration is adjusted based on the time-averaged concentration of CH_4 in the product, using control strategies known in the art to shorten or
15 lengthen the duration to achieve the target CH_4 amount. In a preferred embodiment, the target CH_4 amount is set at an amount that represents between about 1% and about 15% of the hydrocarbonaceous feed carbon. In embodiment (c), the regeneration step duration is of fixed length, at a value that is predetermined to be acceptable for the space velocity of the operation. In one
20 embodiment the present invention, the regeneration step duration is fixed at a duration between about 0.1 second and about 60 seconds and preferably 1.0-30 seconds. In all of these cases, but particularly in embodiment (c), it is preferable to also adjust the regeneration flow rates to increase or decrease the amount of heat added to the bed during the step - in a manner similar to that described with
25 respect to adjustment of duration in embodiment (b), above. In a further embodiment of the present invention, the regeneration step duration is fixed at a duration between about 1 second and about 60 seconds, and the regeneration flow rate is adjusted over time so that the time-average concentration of CH_4 in the reforming product approaches a target CH_4 amount that is set at an amount

that represents between about 1% and about 15% of the hydrocarbonaceous feed carbon.

5 [0035] The reforming zone is now, once again, at reforming temperatures suitable for catalytic reforming.

10 [0036] In the practice of the present invention it is important to operate the two steps of the cycle at different pressures. This is advantageous because it is costly to compress air to high pressure, while it is desirable to have synthesis gas at high pressure. Thus, in a preferred embodiment, the reforming step is carried out at higher pressures than the regeneration step. The pressure swing is enabled because of the large volumetric heat capacity difference between the solid and the gas.

15 [0037] Pressure swing reforming operating temperatures and pressures are given in Table 1.

Table 1		
	Broad Range	Preferred Range
Reforming Step Pressure	2 - 100 atm	5 - 50 atm
Regeneration Step Pressure	1 - 30 atm	2 - 20 atm
Reforming Feed Temperature	20 - 600°C	150 - 450°C
Regeneration Feed Temperature	20 - 600°C	150 - 450°C
Regeneration Peak Bed Temperature	700 - 2000°C	900 - 1600°C

20 [0038] The space velocity of a system is typically expressed on an hourly basis as the standard volumetric gas flow rate of feed divided by the volume of catalyst bed, called gaseous hourly space velocity, or GHSV. Space velocity can also be defined in terms of the hydrocarbon component of feed. As so defined, the GHSV for a methane feed would be the standard hourly volumetric gas flow rate of methane divided by the bed volume. As used herein, the term space

velocity, abbreviated as $C_1\text{GHSV}$, refers to the space velocity of any hydrocarbon feed placed on a C_1 basis. As such, the hydrocarbon feed rate is calculated as a molar rate of carbon feed, and standard volume rate calculated as if carbon is a gaseous species. For example, a gasoline feed having an average carbon number of 7.0 that is flowing at a gaseous flow rate of 1,000NL/hr into a 1.0L bed would be said to have a space velocity of 7,000. This definition is based on feed flow during the reforming step and wherein the bed volume includes all catalysts and heat transfer solids in the reforming and recuperating zones.

[0039] In pressure swing reforming, the space velocity, $C_1\text{GSHSV}$, typically ranges from about 1,000 to about 50,000.

[0040] In a preferred embodiment pressure swing reforming is conducted under bed packing and space velocity conditions that provide adequate heat transfer rates, as characterized by a heat transfer parameter, ΔT_{HT} , of between about 0.1°C to about 500°C , and more preferably between about 0.5°C and 40°C . The parameter ΔT_{HT} is the ratio of the bed-average volumetric heat transfer rate that is needed for reforming, H , to the volumetric heat transfer coefficient of the bed, h_v . The volumetric heat transfer rate that is needed for reforming is calculated as the product of the space velocity with the heat of reforming (on heat per C_1 volume basis). For example, $H=4.9 \text{ cal/cc/s} = 2.2 \text{ cal/cc} * 8000 \text{ hr}^{-1} / 3600 \text{ s/hr}$, where 2.2 cal/cc is the heat of reforming of methane per standard volume of methane, and 8000 is the $C_1\text{GHSV}$ of methane. When the duration of reform and regeneration steps are comparable, the value of H will be comparable in the two steps. The volumetric heat transfer coefficient of the bed, h_v , is known in the art, and is typically calculated as the product of a area-based coefficient (e.g. $\text{cal/cm}^2\text{s}^\circ\text{C}$) and a specific surface area for heat transfer (a_v , e.g. cm^2/cm^3), often referred to as the wetted area of the packing.

[0041] Bed packing materials suitable for use in the pressure swing reforming process include cordierite, aluminum silicate clays, mullite, silica-alumina, zirconia and the like that are stable to at least 1000°C.

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[0042] Figure 2 illustrates one embodiment of the process employing heat exchange. In this embodiment, two pressure swing reforming bed systems are used simultaneously such that one system is reforming while the other is regenerating. The use of multiple beds can provide a continuous flow of reformed product notwithstanding the cyclical operation of each bed. In Figure 2, a first bed (148) is engaged in the step of regeneration, while a second bed (149) is engaged in the step of reforming. Each bed (148 and 149) includes both reforming and recuperating zones. In this embodiment, several sets of valves are used to control the various streams flowing to and from the beds. A first set of valves (157 and 159) controls the flow of hydrocarbon, steam and optional CO₂ feed to the beds, while a second set of valves (152 and 154) control the flow of the product of the reforming step exiting the recuperating zones. The third set of valves (151 and 153) regulate the flow of oxygen-containing gas/fuel and optional non-combusting gas to the beds and the fourth set of valves (156 and 158) control the flow of fluegas exiting the reforming zone.

[0043] In operation, when valves 151, 154, 156, and 159 are open, valves 152, 153, 157, and 158 are closed. With these valve states, oxygen containing gas (162) and fuel (161) enter the bed (148) through valve 151 while fluegas exits the bed (148) through valve 156. Concurrently, the hydrocarbon, steam and optional CO₂ feed enters the second bed (149) through valve 159 while the product of reforming exits this bed (149) through valve 154. At the conclusion of this step, valves 152, 153, 157 and 158 now open and valves 151, 154, 156

and 159 now close, and the cycle reverses, with the first bed (148) reforming the feed and the second bed (149) regenerating the heat.

5 [0044] Turning to Figure 3, which illustrates an embodiment of the present invention, synthesis gas which is produced in the pressure swing reformer (28) is utilized in a hydrocarbon synthesis reactor (29) such as a Fischer-Tropsch (FT) reactor.

10 [0045] The pressure swing reforming process results in the formation of a syngas stream having a $H_2:CO$ ratio of about 3:1. For gas conversion processes it is desirable to have a $H_2:CO$ ratio of about 2:1. Therefore the syngas product of the pressure swing reforming process preferably is subjected to a separation step in which a fraction of the hydrogen is removed in a separator (30) for use in the regeneration step. Because the regeneration may be performed at
15 substantially lower pressure than the reforming step a membrane separator is particularly preferred. As shown in Figure 3, supplemental hydrocarbon, e.g., CH_4 , may be added for fuel balance.

20 [0046] The pressure swing reforming reactor (28) is fed during its reforming step with a combined reforming feed (102), yielding a product syngas (103). During the regeneration step, the regeneration feed (116) enters the pressure swing reformer and fluegas product (117) is produced. The regeneration feed may enter together or as separate fuel and air streams, but is shown as a single combined feed (116) for material balance purposes. Heat exchange is not shown
25 in Figure 3, but is understood to take place as described in this disclosure and otherwise known in the art. Where conditions are given for streams (102,103,116, & 117), the conditions are at point of entry or departure of the pressure swing reformer.

[0047] The syngas product of reforming (103) has a higher H_2/CO than is needed for synthesis, and is directed to a separations step (30) where some of the excess H_2 is removed as stream (105). The remaining syngas (104), having H_2/CO suitable for synthesis, is directed to the hydrocarbon synthesis (HCS) reactor (29). In this example, the hydrocarbon synthesis reaction is catalyzed by a cobalt-based catalyst to produce a paraffinic liquid (106) at high conversion. Although this embodiment is shown as a single reactor, multiple reactors may be employed, as is known in the art. In addition, separation steps are included with the HCS reactor to segregate water and to keep the valuable, high-boiling components in the liquid stream (106) while placing the low-boiling components in a "tail-gas" stream (107). In the present example, the tail gas stream (107) includes all hydrocarbons with 4 carbons or fewer, the majority of which is methane. The HCS reaction is exothermic and thus heat is removed as a heated cooling medium (108). Cooling of HCS reactors is known in the art.

[0048] In the example described (Example 1), a fraction of the CO_2 in the HCS tail gas (107) is removed via separation (31), yielding a concentrated CO_2 stream (109) and a tailgas stream depleted in CO_2 (110). This tailgas stream (110) is a reduced- CO_2 HCS-tailgas, that is combined with fresh natural gas (101) and steam (111) to make the combined reforming feed (102). In this example, the steam includes a small amount of steam that is used to purge the pressure swing reformer bed of hydrocarbons and syngas at the end of the reforming step. It is understood that some compression is required in the syngas loop, as each of the steps extracts some pressure drop, such that the recycled syngas (110) will be at lower pressure than the reformer feed (102) in the absence of compression. Compression is least expensive if applied to the final tailgas (110), whose volume is the smallest.

[0049] Regeneration of the pressure swing reformer is carried out, in the present example, using primarily the hydrogen stream (105) that is removed in the hydrogen separator (30). In the general use of this invention, some of this hydrogen may be taken as a purified hydrogen stream (112) for use in other applications. For example, the H₂ might be used in hydrocarbon upgrading steps. Also, in general, the heat of combustion of the hydrogen-containing stream (112) may not exactly match what is required for regeneration, and thus may require hydrogen purge (112) or supplemental fuel (113). The present example includes zero hydrogen removal (112) and a small amount of supplemental fuel (113). The combined regeneration feed (116) in the present example is composed of hydrogen fuel (105), a small amount of supplemental natural gas (113), fresh air (114) and recycled fluegas (115). Fluegas is recycled, in this embodiment, to reduce the oxygen content of the regeneration streams. The final tailgas emitted to atmosphere (118) is the regeneration product (117) minus the material recycled (115).

[0050] The material balance for this example 1 embodiment of the present invention is shown as a table of key streams in Table 2. As can be seen, the material balance of Table 2 has a regeneration pressure of about 2 atm. Such pressure is suitably provided by air blower equipment. Regeneration flue gas (118) may be directed to a gas expander to recover work energy that may be used to drive the air blower. In one embodiment of the present invention, this blower-expander pair is mechanically coupled to provide for improved cost or efficiency. In such an embodiment, the PSR regeneration pressure is preferably from about 2 to about 10 atm (absolute).

[0051] In another embodiment of the present invention, this blower-expander function is provided by integrating the PSR regeneration system with a Gas Turbine. Gas turbines operate by compressing air to moderate pressure (7-30

atm), combusting a fraction of that air with fuel such that the combined stream of air and combustion product is heated to elevated temperature (900-1300C), and then expanding the combined stream in a turbine resulting in mechanical power sufficient to drive the compressor and have residual power that may be used for electricity manufacture or other purposes. It is known in the art that hot compressed air can be withdrawn from gas turbines, used in outside processes, and returned with some composition and condition changes to the turbine to fulfil its role as combustion diluent and expansion fluid.

[0052] In a preferred embodiment of the present invention, the regeneration fresh air (114) is provided as air that is extracted from a gas turbine, and the regeneration flue gas (118) is returned to the gas turbine to fulfil the gas turbine needs for combustion diluent and expansion fluid. The gas turbine power output may be used to co-produce electricity or to power the electrical and driver needs of the overall process. A material balance for this example 2 embodiment is shown as table 3. This example is prepared using air flows and conditions that are consistent with integration with a General Electric Frame 9 gas turbine. However, any turbine may be used, the choice of turbine being a matter of scale, process economics, and desired proportions of power to liquid product.

[0053] In yet another embodiment, byproducts and unconverted syngas is recycled, as shown in Figure 4, to the pressure swing reformer without removal of any of the contained CO₂. In addition, this embodiment uses excess air for regeneration, instead of the air/fluegas mixture of example 1, and this embodiment uses the steam generated in cooling the synthesis reactor directly as reactant for reforming.

[0054] The pressure swing reforming reactor (28) is fed during its reforming step with a combined reforming feed (102), yielding a product syngas (103).

During the regeneration step, the regeneration feed (116) enters the pressure swing reformer and fluegas product (117) is produced. The regeneration feed may enter together or as separate fuel and air streams, but is shown as a single combined feed (116) for material balance purposes. Heat exchange is not shown
5 in Figure 4, but is understood to take place as described in this disclosure and otherwise known in the art. Where conditions are given for streams (102, 103, 116, & 117), the conditions are at point of entry or departure of the pressure swing reformer.

10 **[0055]** The syngas product of reforming (103) has a higher H_2/CO than is needed for synthesis, and is directed to a separations step (30) where some of the excess H_2 is removed as stream (105). The remaining syngas (104), having H_2/CO suitable for synthesis, is directed to the hydrocarbon synthesis (HCS) reactor (29). In this example, the hydrocarbon synthesis reaction is catalyzed by
15 a cobalt-based catalyst to produce a paraffinic liquid (106) at high conversion. Although this embodiment is shown as a single reactor, multiple reactors may be employed, as is known in the art. In addition, separation steps are included with the HCS reactor to segregate water and to keep the valuable, high-boiling components in the liquid stream (106) while placing the low-boiling components
20 in a "tail-gas" stream (107). In the present example, the tail gas stream (107) includes all hydrocarbons with 4 carbons or fewer, the majority of which is methane. The HCS reaction is exothermic and thus heat is removed as a heated cooling medium (108). In this embodiment, the cooling medium is water, which, upon absorbing heat from the HCS reaction, is converted to ~10 atm
25 steam (108).

[0056] In the example shown, HCS-tailgas (107) is combined with fresh natural gas (101) and steam (111) to make the combined reforming feed (102). In this example, the source of the steam (111) is the steam (108) generated by

cooling the HCS reactor. The amount of steam (111) used in pressure swing reforming includes a small amount of steam that is used to purge the pressure swing reformer bed of hydrocarbons and syngas at the end of the reforming step. It is understood that some compression is required in the syngas loop, as each of
5 the steps extracts some pressure drop, such that the recycled syngas (110) will be at lower pressure than the reformer feed (102) in the absence of compression. Compression is least expensive if applied to the final tailgas (110), whose volume is the smallest.

10 [0057] Regeneration of the pressure swing reforming is carried out, in the present example, using primarily the hydrogen stream (105) that is removed in the hydrogen separator (30). In the general use of this invention, some of this hydrogen may be taken as a purified hydrogen stream (112) for use in other applications. For example, the H₂ might be used in hydrocarbon upgrading
15 steps. Also, in general, the heat of combustion of the hydrogen-containing stream (112) may not exactly match what is required for regeneration, and thus may require hydrogen purge (112) or supplemental fuel (113). The present example includes zero hydrogen removal (112) and a small amount of supplemental fuel (113). The combined regeneration feed (116) in the present
20 example is composed of hydrogen fuel (105), a small amount of supplemental natural gas (113), and fresh air (114). The final flue gas emitted to atmosphere is the regeneration product (117).

[0058] The material balance for this example 3 embodiment of the present
25 invention is shown as a table of key streams in Table 4.

[0059] As is known, the Fischer-Tropsch process is exothermic and water is used to control the temperature with steam (108) being produced. As shown in Figure 3, at least part of this steam (108), may be used in the reformer (28). As

will be readily appreciated the steam produced in cooling the hydrocarbon synthesis reactor may be at a lower pressure than the desired reforming pressure of the pressure swing reformer in which event the pressure swing reformer will be operated at the pressure at which the steam is produced or the steam may be
5 compressed to a higher pressure.

[0060] In yet another embodiment shown in Figure 5 steam (108) recovered from the hydrocarbon synthesis reactor (29) is utilized to provide the power needed to compress the steam for the syngas reactor. In this embodiment, low
10 pressure steam (108) from the hydrocarbon synthesis reactor is divided between a stream (130) to be expanded and a stream (133) to be compressed. In this embodiment the stream to be expanded is heated in a superheater (135) before expanding in a turbine (32) to produce shaft power. The shaft power turns compressor (33), which compresses steam (133) to become a higher pressure
15 stream (134) that may be used in the reforming step.

[0061] In a preferred embodiment, the bed packing material in the pressure swing reformer is designed so that regeneration can be carried out with a pressure drop of less than 2 atm, more preferably less than 1 atm. Preferred
20 packing materials for this embodiment are designed to pass large quantities of gas with small pressure drops. Preferred material shapes include honeycomb monoliths and wall-flow monoliths. Honeycomb monoliths are well known in the art, for example, as described in US 3,885,977. Honeycomb monoliths derive their low pressure drop from the long straight channels oriented in the
25 direction of flow. Wall-Flow monoliths are also known in the art, for example, as described in US 4,276,071. Most commonly, wall flow monoliths are fabricated as derivatives of honeycomb monoliths, by plugging alternate channel ends, as described in US 4,509,966. Wall-Flow monoliths derive their low pressure drop from the long straight channels oriented in the direction of flow,

but add a large measure of heat transfer area by forcing the flow through the thin walls of the monolith.

[0062] The advantage of using a honeycomb or wall-flow monolith in the
5 present invention is that, for a given level of heat transfer, these shapes can be
operated at a much higher velocity than would be possible with a bed of
particulate packing. Hydrocarbon synthesis processes are economically favored
by operations at very large scale. At very large scale, reforming volume must
also be large. It is desirable to provide this volume by increasing bed volume in
10 all dimensions; diameter and length, thus providing the most economical bed
designs. Since pressure drop increases with length, the very largest scales
require the lowest pressure-drop designs. Preferred honeycomb monoliths for
the present invention will have channel densities that range from about 100
cells/in² to about 1600 cells/in² (15-250 cells/cm²).

Table 2: Flow Rates (kg/hr) and PSR Conditions for Selected Key Streams in Figure 3 and Example 1.

Stream	Fresh NG	Ref Fd	Ref Prod	Regen Fd	Regen Out	Adj. SG (dry basis)	HCS Liq.	HCS Tailgas (dry basis)	RCY Tailgas (dry basis)
101	102	103	116	117	104	106	107	110	
PSR P, atm	25	25	2.5	2					
PSR T, °C	400	435	400	500					
NG (C1-C4)	312,722	344,096	5,166	2,985	0	5,166		31,374	31,374
H2O		916,474	434,564	1,086,422	1,574,780				
H2		4,724	134,126	44,173	0	89,942		4,724	4,724
CO		29,838	596,769	0	0	596,769		29,838	29,838
CO2		98,327	136,177	23,280	31,488	136,177		136,177	98,327
N2				4,657,947	4,651,855				
O2				367,115	4,600				
Liquids (C5+)							262,304		

Table 3: Flow Rates and Conditions for selected key streams in Figure 3 and Example 2.

	Fresh Nat. Gas	Reform Feed	Reform Product	Regen Feed	Regen Product	Extract Air	Recycle	Turbine Return	Syngas /HCS Fd	HCS Liquid	Recycle
Stream	101	102	103	116	117	114	115	118	104	106	110
P, atm. Abs		25.0	25.0	12.5	12.2	12.6		12.2			
T,C		215	415	385	430						
kg/hr											
NG (C1-C4)	201,825	222,066	3,328	3,973					3,328		20,241
H2O		609,458	299,598	711,139	1,029,480		711,139	318,342	4,127		
H2		3,073	86,698	28,604					58,044		3,049
CO		19,247	385,127						385,127		19,256
CO2		64,695	90,197	27,810	38,411		27,810	10,601	90,197		64,695
N2				3,097,679	3,074,824	808,176	2,289,503	785,321			
O2				245,522	2,619	245,522		2,619			
Liquids(C5+)										169,279	

